

PATENT SPECIFICATION

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(54) POLYSILOXANE POLYMERS AND CONTACT LENS AND OTHER BIOMEDICAL ARTICLES FORMED THEREFROM

(71) We, BAUSCH & LOMB INCORPORATED, a corporation organised and existing under the laws of the state of New York, United States of America of 1400 North Goodman Street, Rochester, N.Y. 14602, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel polysiloxane polymers and to shaped biomedical articles, particularly contact lenses, formed therefrom.

The polysiloxane polymers of the present invention are formed by polymerizing one or more poly(diorganosiloxane) or linear poly(organosiloxane) monomers α,ω -terminally bonded through divalent hydrocarbon groups of at least three carbon atoms to activated unsaturated groups (as herein defined), optionally with one or more free-radical polymerizable co-monomers, to form a cross-linked three-dimensional polymeric network.

By "activated unsaturated group" as this term is used herein is meant that the unsaturated group is one which has a substituent which functions through resonance to increase the free radical stability of the monomer. These activated unsaturated groups become polymerized to form a polymer with a crosslinked three-dimensional network. Preferably, the activating groups present are such that the monomers lend themselves to polymerization under mild conditions, such as ambient temperatures.

The present polysiloxane polymers are generally useful in the fabrication of shaped articles for biomedical use, and in particular preferred polysiloxane polymers of the present invention may be employed to make optical products such as contact lenses and intraocular implants with improved properties. Advantageously, contact lenses with desirable properties such as oxygen transportability, hydrolytic stability, biological inertness, transparency and improved strength without the use of fillers can be obtained in accordance with the present teachings. Such contact lenses can be, as commonly referred to, either "hard" or "soft", this hardness or softness being a function of polymer molecular weight and/or the use of comonomers. "Soft" contact lenses are usually preferred.

The use of siloxane polymers for the fabrication of optical contact lenses is desirable. The desirability is due to the high oxygen transportability and generally the relative softness of polysiloxanes. The tear strength and tensile strength of polysiloxane elastomers, however, are generally poor and as a result fillers are employed to increase the strength of the elastomers. In U.S. Patent Nos. 3,996,187,



3,996,189, 3,341,490 and 3,228,741 there are described contact lenses fabricated from poly(organosiloxanes) containing fillers. The tear strength and tensile strength of the contact lenses made from the preferred polymers of the present invention are of sufficient strength that no fillers are required.

U.S. Patents 3,996,187 and 3,996,189, as mentioned above, disclose contact lenses made from reinforced polysiloxanes. The lenses contain various polysiloxanes with index of refractions similar to the silica filler so that an optically clear silica filled silicone elastomer can be formed from aryl and alkyl siloxanes. The material contains from 5 to 20 percent silica. The silica is used, as mentioned, for strength. In contrast, the contact lenses formed from the instant polymers need contain no fillers for strength.

U.S. Patent 3,341,490 discloses contact lenses made from blends of siloxane copolymers containing reinforcing silica fillers. As mentioned, the contact lenses of the instant invention need contain no fillers.

U.S. 3,228,741 discloses contact lenses made from silicone rubber particularly hydrocarbon substituted polysiloxane rubber. This silicone material contains fillers such as pure silica to control flexibility, pliability and resiliency of the lenses. Contact lenses formed from the instant polymers require no fillers.

U.S. Patent 3,808,178 discloses a polymeric material containing a polymethacrylate backbone with relatively short poly(organosiloxane) ester side chains on the backbone polymer. There is no cross-linking involved in '178 since the monomers disclosed in '178 are monofunctional i.e. have only one functional group on each monomer. In order to get cross-linking in '178 it is taught at column 5 of '178 that different monomers must be added for cross-linking which have more than one functionality. However, in the instant invention cross-linking is obtained since each siloxane monomer is difunctional i.e. each monomer contains two functional groups, (most preferably two methacrylate groups, as explained below), which results in cross-linking. Furthermore, contact lenses made from the polymers disclosed in '178 would not transport oxygen sufficiently whereas contact lenses made from the instant polymers will transport oxygen sufficiently to meet the requirements of the human cornea.

U.S. Patent 3,518,324 teaches vulcanizing to make silicone rubber whereas the instant invention is concerned with contact lenses made from polymerizing specific monomers.

U.S. Patent 2,770,633 discloses 1,3 - bis(4 - methacryloxybutyl)tetramethyl disiloxane, one of the preferred monomers used in the instant invention. This is taught at column 1, line 63 of '633 when R equals vinyl. However, '633 teaches only the monomer whereas the instant invention teaches not the monomer but the polymer. In fact '633 would not want the monomer to polymerize since it would not perform its function as a lubricant if polymerized.

U.S. Patent 2,906,735 teaches a reaction between an alkyl siloxane and acrylic acid or a methacrylic acid resulting in a disiloxane terminated by acrylate groups. '735 does not teach the polymers of the instant invention.

U.S. Patent 2,922,807 discloses disiloxanes having acryloxy or methacryloxy groups attached to the silicone through a divalent alkylene radical of from 2 to 4 carbon atoms.

None of the above patents teach the instant invention much less the most preferred embodiment of the instant invention which is 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane reacted with, preferably, octamethyl cyclotetrasiloxane, to form the preferred monomer. This preferred monomer is then polymerized to the preferred cross-linked polymer of the instant invention. Furthermore, and most importantly, none of the prior art teaches contact lenses made from the instant polymers.

U.S. 3,763,081 discloses, in pertinent part, the polymerization of an unsaturated siloxane which is somewhat difficult to polymerize since a double bond in this type of monomer generally is not very active. One must use both high temperatures and a peroxide catalysis or a platinum catalysis in order to complete this type of reaction. See, for example, '081 at column 4 lines 55-46. In the instant reaction the monomeric materials are referred to specifically as having activated unsaturated groups bonded through a divalent hydrocarbon group to the siloxane whereas '081 has no activated unsaturated groups bonded to the siloxane.

U.S. Patent 2,865,885 in pertinent part teaches a vinyl group which is not activated as shown in column 1 lines 25-30 of '885. The reason '885's double bond is not "active" in the sense defined in the instant application is that the double

bond is bonded to either sulfur or oxygen. In the instant invention this same position would have, for example a



carbonyl group. This would make the double bond active as defined in the instant application. Therefore, in '885 since the reactivity ratios are so different i.e. the double bond is not active in '885 as defined in the instant invention, it would be very difficult to get an acceptable copolymerization reaction using the formulae of '885 as compared to the active double bond in the instant invention which easily copolymerizes. In the instant invention the unsaturated eg vinyl group is "activated" to facilitate free radical polymerization. The formula given at column 1, lines 25—30 of '885 does not lend itself to free radical polymerization due to the lack of resonance but rather it lends itself to ionic polymerization due to the polar nature of the substituents. Therefore, it would be extremely difficult, if at all possible, for '885 to form the compounds of the instant invention. Also the compounds formed in '885 are not hydrolytically stable because of the presence of the silicon-nitrogen bond in the formula. The instant invention cannot use a hydrolytically unstable compound. Furthermore, the products of this hydrolysis in '885 could be injurious to the human eye particularly the amines. Also at column 3 of '885 the linkage is an amine linkage to the double bond and in the instant invention this linkage is always an alkyl. Therefore, '885 does not teach the instant monomers.

U.S. Patent 2,793,223 in pertinent part at Example 5 at column 3, lines 30—41 teaches that a phenyl group is attached to the siloxane. Therefore, that material would be very hard and opaque. This would be unsuitable for contact lens which must be transparent. Furthermore, contact lenses made from the polymers made from the monomers disclosed in '223, because of the presence of the phenyl group on the siloxane as shown in Example 5 of '223, would not transport oxygen sufficiently whereas contact lenses made from the instant polymers would transport oxygen sufficiently to meet the requirements of the human cornea.

The present invention provides materials which can be usefully employed for the fabrication of prostheses such as heart valves and intraocular lenses, as optical contact lenses or as films. More particularly, the instant invention concerns contact lenses.

Thus, in one embodiment of this invention there is provided a fillerless, oxygen transporting, hydrolytically stable, biologically inert, transparent contact lenses formed from a polysiloxane polymer of this invention as defined above.

When the statement is made "a poly(diorganosiloxane) or linear poly(organosiloxane) terminally bonded through a divalent hydrocarbon group of at least three carbon atoms to an activated unsaturated group" it is meant that the siloxane is attached to a divalent hydrocarbon group of at least three carbon atoms, such as propylene and then at each end of the resulting residue is attached an activated unsaturated group such as methacryloxy. Then when the monomers are polymerized (i.e. cross-linked) the activated unsaturated groups are polymerized (free radical polymerization) then the monomers form three dimensional polymers which is the material of which a contact lens or other shaped biomedical article can be made.

The monomers employed in accordance with this invention, as a result of the presence of the activated unsaturated groups, are readily polymerized to form three dimensional polymeric networks which permit the transport of oxygen and are optically clear, strong and can be made, as desired, soft or hard.

When the term "monomer" is used herein we mean to include polysiloxanes end-capped with activated unsaturated groups. The process of lengthening the siloxane portion of the monomer is referred to herein as siloxane ring insertion. The chain length of the polysiloxane center unit of the monomers may be as high as 800 or more.

When the term "polymerization" is used herein we refer to the polymerization of the double bonds of the polysiloxanes end capped with activated unsaturated groups which results in a cross-linked three dimensional polymeric network.

The relative hardness (or softness) of the contact lenses formed from the polymers of this invention can be varied by decreasing or increasing the molecular weight of the monomeric poly(organosiloxane) end-capped with the activated

unsaturated groups or by varying the amount of any comonomer. As the ratio of organosiloxane units to end cap units increases the softness of the material increases. Conversely, as this ratio decreases the rigidity and hardness of the material increases. The present contact lenses may be formed by spin-casting, if desired, such as taught in U.S. patent 3,408,429.

In one embodiment of this invention there are provided copolymers wherein the poly(organosiloxane) monomer is copolymerized with one or more monomers which, for example, can be one of the lower esters of acrylic or methacrylic acid, or a styryl, allyl or vinyl compound. The copolymers are in the form of three dimensional networks which are clear, strong and can be usefully employed in providing films, and shaped bodies such as contact lenses.

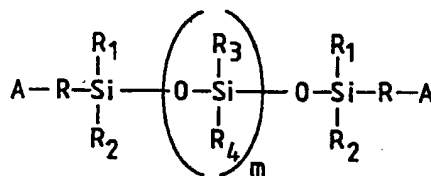
Suitably, the novel copolymers of this invention can comprise 10 to 90 parts by weight of one or more of the organosiloxanes described herein and 90 to 10 parts by weight of the polymerizable co-monomers. The preferred contact lenses formed from these copolymers are fillerless, oxygen transporting, flexible, hydrolytically stable, biologically inert, transparent, resilient and soft.

The three-dimensional network polymer products of this invention are readily prepared by means of conventional free radical polymerization techniques. For example, the monomers of organosiloxane, alone or in the presence of comonomers, together with 0.05 to 2% by weight of a free radical initiator may be heated to a temperature of 30°C to 100°C to initiate and complete the polymerization. The polymerizable monomers i.e., the poly(organosiloxane), with or without comonomers, can preferably be subjected at room temperature to irradiation by UV light in the presence of suitable activators such as benzoin, acetophenone, or benzophenone for a sufficient time so as to form a three dimensional polymer network.

The polymerization can be carried out directly in contact lens molds, or the polymer can be cast into discs, rods or sheets which can then be fabricated to a desired shape. Preferably the polymerization is carried out while the material is being spin cast, such as taught in U.S. patent 3,408,429.

As is well established, the oxygen transportability of polysiloxanes is substantially greater in comparison to the conventional contact lens polymers such as polymethyl methacrylate (PMMA) or polyhydroxyethylmethacrylate (HEMA). The oxygen transportability of the materials of this invention can be varied by altering the percentage of siloxane units. For example, a high percentage of siloxane units results in a product more capable of transporting oxygen as compared with a lower percentage of siloxane units which results in a material with less ability to transport oxygen.

In accordance with one embodiment of this invention, the linear poly(organosiloxanes) or poly(diorganosiloxane monomers employed are of the formula:

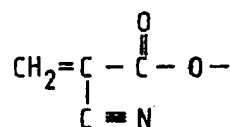


wherein A is an activated unsaturated group (as hereinbefore defined), R is a divalent hydrocarbon radical having from 3 to 22 carbon atoms, R₁, R₂, R₃ and R₄ can be the same or different and each is one of a monovalent hydrocarbon radical or a halogen substituted monovalent hydrocarbon radical each having from 1 to 12 carbon atoms and m is 0 or greater.

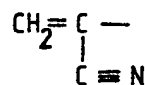
Desirably m can be in the range of 50 to 200. However, the range of m can be greater, eg 50 to 800. Indeed, m can be greater than 800. Should one desire to obtain a harder contact lens m should be less than 25. To produce softer contact lenses, m should be more than 25 and preferably 50 to 800.

Preferably A, the activated unsaturated group, is one of

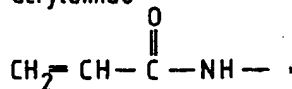
2 - cyanoacryloxy



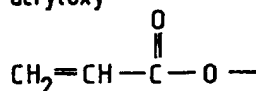
acrylonitril



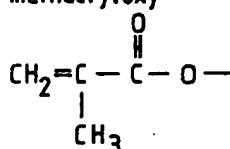
acrylamido



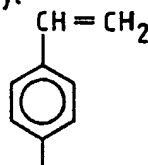
acryloxy



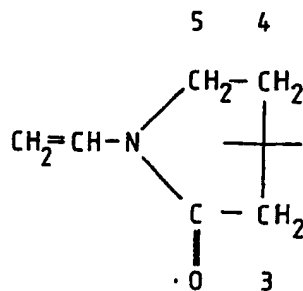
methacryloxy



styryl



and
N - vinyl - 2 - pyrrolidinone - x - yl wherein x may be 3, 4 or 5 corresponding to
the formula



having one hydrogen atom removed from positions 3, 4 or 5.

More preferably A is acryloxy or methacryloxy. However, other groups containing activated unsaturation can be readily employed, such groups being well known to those skilled in the art. Most preferably A is methacryloxy or acrylamido.

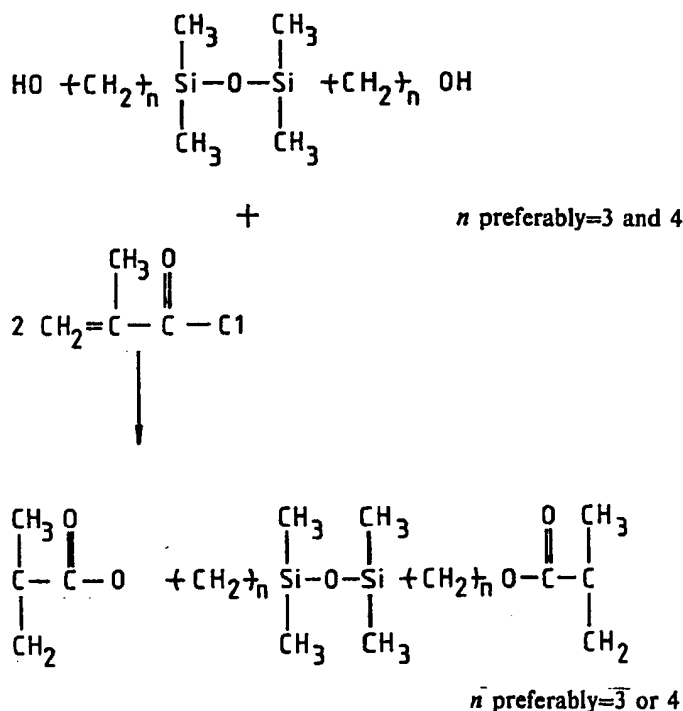
R may be preferably an alkylene radical. Therefore, preferably R is propylene, butylene, pentamethylene, hexamethylene, octamethylene, dodecylmethylenes,

hexadecylmethylene and octadecylmethylene; arylene radicals such as phenylene, bi-phenylene and the corresponding alkylene and arylene radicals. More preferable R is an alkylene radical having 3 or 4 carbon atoms, e.g. butylene. Preferably, R₁, R₂, R₃ and R₄ are alkyl radicals having from 1 to 12 carbon atoms, e.g., methyl, ethyl, propyl, butyl, octyl, and dodecyl; cycloalkyl radicals, e.g., cyclopentyl, cyclohexyl, and cycloheptyl; mononuclear and binuclear aryl radicals, e.g., phenyl, and naphthyl; aralkyl radicals, e.g., benzyl, phenylethyl, phenylpropyl, and phenylbutyl; alkaryl radicals, e.g., tolyl, xylyl, and ethylphenyl; haloaryl radicals such as chlorophenyl, tetrachlorophenyl, and difluorophenyl; halo substituted lower alkyl radicals having up to four alkyl carbon atoms such as fluoromethyl and fluoropropyl. More preferably R₁, R₂, R₃ and R₄ are methyl radicals and phenyl radicals; most preferably R₁, R₂, R₃ and R₄ are methyl radicals.

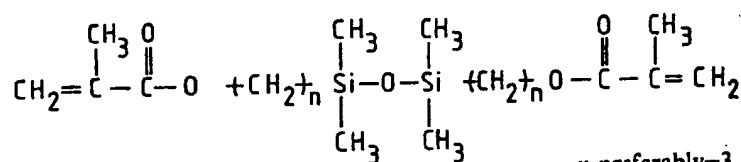
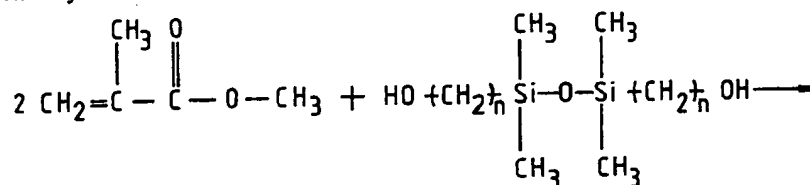
The activated unsaturated group end-capped polysiloxanes, i.e. monomers, employed in this invention can be prepared by equilibrating the appropriately substituted disiloxane, for example, 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane, with a suitable amount of a cyclic diorganosiloxane, e.g., hexamethyl cyclotrisiloxane, octaphenyl cyclotetrasiloxane, hexaphenylcyclotrisiloxane, 1,2,3 - trimethyl - 1,2,3 - triphenyl - cyclotrisiloxane, or 1,2,3,4 - tetramethyl - 1,2,3,4 - tetraphenylcyclotetrasiloxane in the presence of an acid or base catalyst. The degree of softness, the physical properties such as tensile strength, modulus and percent elongation will determine the amount of cyclic diorganosiloxane equilibrated with the disiloxane. By increasing the amount of cyclic siloxane one increases *m*.

The reaction between a cyclic diorganosiloxane and disiloxanes, although not specifically disclosed for the disiloxanes employed in this invention as to provide the activated unsaturated groups as the end caps for polysiloxanes, is a conventional reaction and described by, for example, Kojima et al. Preparation of Polysiloxanes Having Terminal Carboxyl or Hydroxyl Groups, J. Poly. Sci., Part A-1, Vol. 4, pp 2325-27 (1966) or U.S. Patent No. 3,878,263.

The following reactions represent the formation of the most preferred materials of the instant invention. 1,3 - bis(hydroxyalkyl) tetramethyl disiloxane dimethacrylates are prepared by the following reactions: (1) esterification with acryloyl or methacryloyl chloride or anhydride. For example, the following is with methacryloyl chloride:



(2) Another most preferred method of preparing 1,3 - bis(hydroxyalkyl) tetramethyl disiloxane dimethacrylates is by transesterification with methyl methacrylate:

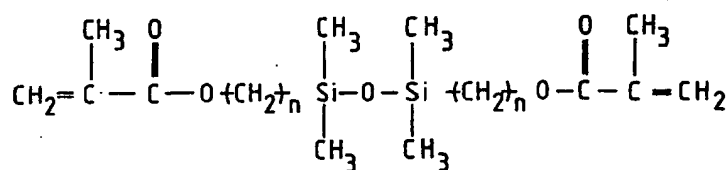


n preferably=3 or 4

5

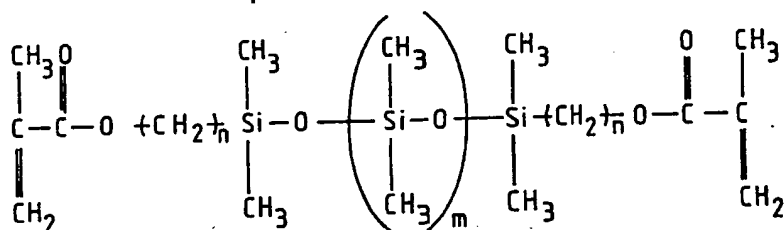
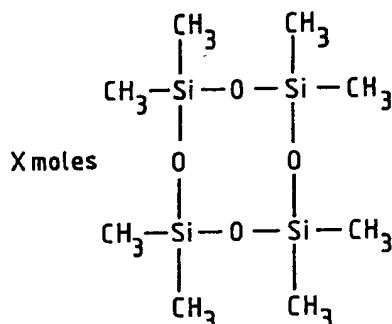
Then the number of siloxane groups between the two methacrylate caps can be increased from 2 to $2+4X$ by a ring opening insertion reaction with X moles of octamethyl cyclotetrasiloxane as follows:

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+

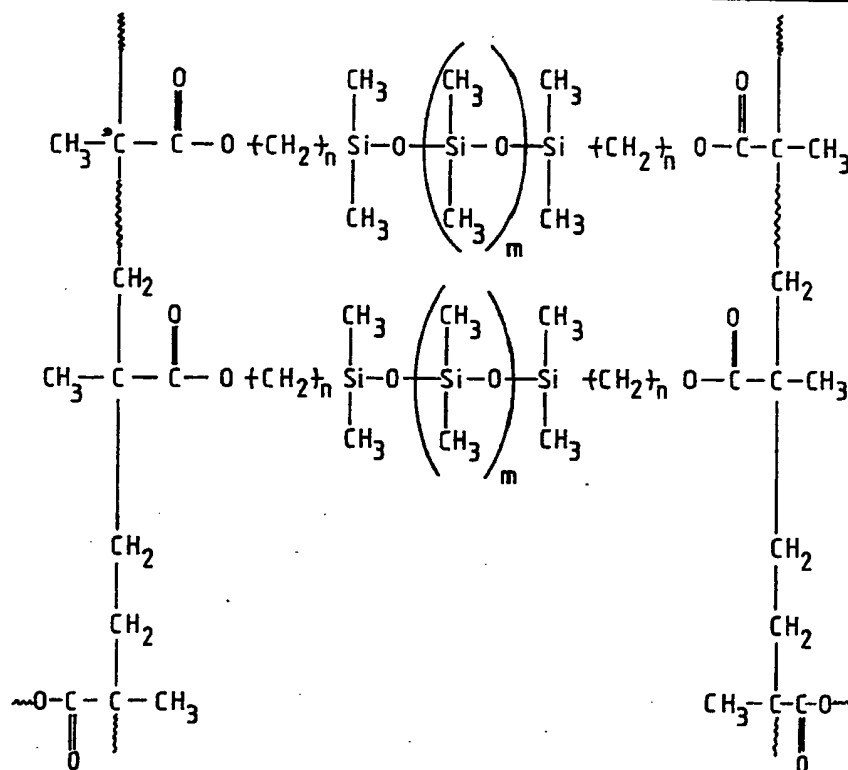
n preferably=3 or 4



n preferably=3 or 4

m preferably=50 to 800
(cross linking/polymerization)

(three dimensional network)



n preferably=3 or 4
 m preferably=50 to 800

5 The linear poly(organosiloxanes) or poly(diorganosiloxanes) α, ω terminally bonded through a divalent hydrocarbon group to an activated unsaturated group i.e. the siloxane monomers used herein, are generally clear, colorless liquids whose viscosity depends on the value of m . These monomers can be readily cured to cast shapes by conventional methods such as UV polymerization, or through the use of free radical initiators plus heat. Illustrative of free radical initiators which can be employed are bis(isopropyl) peroxy dicarbonate, azobisisobutyronitrile, acetyl peroxide, lauroyl peroxide, decanoyl peroxide, benzoyl peroxide, and tertiarybutyl peroxy pivalate. 10

In order to further control the properties of the polymers of the instant invention one can polymerize a mixture of the siloxane monomers comprising monomers having a low value of m and monomers having a high value for m . When m has a low value i.e., below 25, the resulting polymers, eg contact lenses, are relatively hard, oxygen transporting, hydrolytically stable, biologically inert, transparent and do not need fillers to improve the mechanical properties. The monomers have a relatively low molecular weight and as a result the viscosity is low enough e.g. about 3 centistokes so that the lenses may be made easily by spin casting. When m has a relatively high value i.e., above 25, the resulting contact lenses i.e. polymers, become relatively soft, oxygen transporting, flexible, hydrolytically stable, biologically inert, transparent, resilient, and do not need fillers to improve the mechanical properties. The monomers should have preferably a molecular weight low enough so that the viscosity is low enough to spin cast the monomers e.g. 175 stokes or below measured in Gardner viscosity tubes. Preferably m is 50 to 800. 15 20 25

In accordance with one embodiment of this invention there are provided copolymers of monomers which are linear poly(organo-siloxanes) or poly(diorganosiloxanes) terminally bonded through a divalent hydrocarbon group to an activated unsaturated group copolymerized a polymerizable monomer which readily polymerizes by free radical polymerization and preferably is a monomer 30

containing an activated vinyl group. Through the addition of comonomers one can enhance particular desirable properties. For example, buttons fabricated from copolymers of the siloxane monomers tetrahydrofurfuryl methacrylate can be more easily lathed into contact lenses as compared with buttons made from the monomeric siloxanes alone. Wettability of contact lenses fabricated from the polysiloxanes can be substantially increased by copolymerizing the instant siloxane monomers with N-vinyl pyrrolidone.

Illustrative of comonomers which can be usefully employed in accordance with this invention are:

The derivatives of methacrylic acid, acrylic acid, itaconic acid and crotonic acid such as:

methyl, ethyl, propyl, isopropyl, n-butyl, hexyl, heptyl, aryl, allyl, cyclohexyl, 2-hydroxyethyl, 2 or 3-hydroxypropyl, butoxyethyl, methacrylates; and propyl, isopropyl, butyl, hexyl, 2-ethyl hexyl, heptyl, aryl, acrylates; and propyl, isopropyl, butyl, hexyl, 2-ethyl hexyl, heptyl, aryl, itaconates; and propyl, isopropyl, butyl, hexyl, 2-ethyl hexyl, heptyl, aryl, crotonates.

Mono or di esters of the above mentioned acids with polyethers of the below general formula may be used:



wherein n is 1 to 12, preferably 2 or 3, and q is 2 to 6 preferably 2 to 3.

Other comonomers may include:

styryls, such as styrene, divinyl benzene, vinyl ethyl benzene, and vinyl toluene.

Allylic monomers, such as, di allyl diglycol dicarbonate, allylcyanide, allyl chloride, diallyl phthalate, allyl bromide, diallyl fumarate and diallyl carbonate may be used.

Nitrogen containing monomers can be also used, such as:

n-vinyl pyrrolidone, and 3-oxybutyl acrylamide.

The lower the value of m in the formula for the instant monomers the more compatible are the siloxane monomers with the above mentioned comonomers.

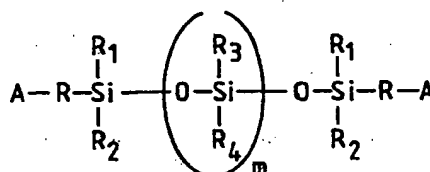
The advantages of using the contact lenses of the instant invention which are made from the preferred polymers disclosed herein are numerous. For example, (1) the advantages of using activated vinyl terminal groups to cure the siloxane material are (a) the high reactivity systems permit rapid cure at room temperature if suitable initiators are used. Room temperatures are preferred. This is desirable since the preferred method of casting is spin casting. (b) No fillers are needed to get useful physical strength as is common with most silicone resins. This is desirable since the use of fillers requires that other possibly undesirable materials be added to the composition in order to correct the refractive index. (2) Furthermore, the contact lenses made from the polymers of the instant invention can be oxygen transporting. The human cornea requires about 2×10^{-8} cm³/(sec. cm² atm.) of oxygen through the contact lens as reported by Hill and Fatt, American Journal of Optometry and Archives of the American Academy of Optometry, Vol. 47, p. 50, 1970. When m is at least about 4 the chain of siloxane is long enough in the instant composition to exceed the oxygen transportability requirements of the cornea. However, in specific situations m may be as low as 0. Because of the unique properties of the polymers of the instant invention m may be great enough to allow the manufacture of contact lenses having sufficient oxygen transportability and at the same time desirable properties of elasticity, tear resistance, flexibility, resilience and softness.

The oxygen transportability was determined by a special test procedure described in conjunction with Example 9 herein. (3) These lenses are hydrolytically stable meaning that when the contact lenses are placed into an aqueous solution, e.g., in the eye, or during the disinfecting step, i.e. water plus heat, the lenses will not change in chemical composition, i.e. hydrolyze, which would cause the lenses to change shape resulting in an undesirable change in optics.

(4) The more preferred contact lenses of the instant invention are also resilient, by which is meant that after the lenses have been deformed the lenses will return quickly to their original shape. (5) The lenses are preferably made by spin casting, e.g. by the method as disclosed in U.S. 3,408,429. Monomers which have too high a viscosity cannot be spin cast. However, generally the higher the molecular weight of the monomers the longer the chain length, i.e. the larger the value of m , and as a consequence the more desirable the properties are for the

preferred contact lenses of the instant invention, made from these monomers. The longer the chain length and the higher the molecular weight the higher the viscosity of the monomers. However, if spin casting is to be used the viscosity of the monomers must be such that these materials can be spin cast. The monomers used in the instant invention can have molecular weights high enough to give all the desirable properties when polymerized but low enough to be spin cast while still in the monomeric form. The preferred weight average molecular weight is from 4,000 to 60,000 for the monomers used in the instant invention. (6) The most preferred contact lenses of the instant invention should be soft, ie they should have a Shore hardness of 60 or below on the A scale, preferably in the range 25 to 35. (7) The preferred contact lenses of the instant invention should be flexible, meaning that the contact lens is capable of being folded or bent back upon itself without breaking.

The most preferred contact lens of the instant invention is a fillerless, oxygen transporting, flexible, hydrolytically stable, biologically inert, transparent, resilient, soft, polymeric contact lens comprising a poly(diorganosiloxane) or linear poly(organosiloxane) α, ω -terminally bonded through a divalent hydrocarbon group of at least two carbon atoms to an activated unsaturated group and having the formula:



wherein A is methacryloxy or acryloxy, R is an alkylene radical having 3 or 4 carbon atoms and m is from 50 to 800.

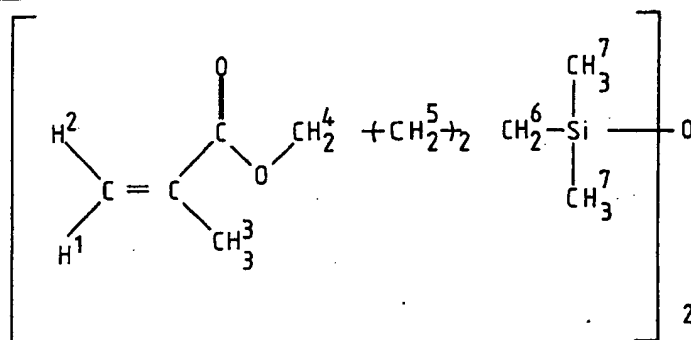
The most preferred contact lenses of the instant invention have a tensile modulus of elasticity of 400 g/mm² or less. Both the Shore hardness and modulus are related to the comfort of the lenses to the wearer when used on the human eye.

Another advantage of the preferred soft contact lenses of the instant invention is that they can be made large enough to cover the entire cornea of the eye resulting in more comfort. Hard contact lenses, such as PMMA lens, have to be made smaller due to their poor oxygen transportability. Furthermore, the larger the lenses, the easier it is to locate the optical center of the lenses. The larger the lens the easier it is to maintain the optical axis which is required in making special lenses for people with particular eye problems, e.g., for those persons with astigmatism. Another advantage of the preferred soft lenses of the instant invention is that they have a softness similar to HEMA lenses but in addition, and most importantly, are more oxygen permeable, i.e. are capable of transporting more oxygen. HEMA lenses are not oxygen permeable or capable of transporting oxygen to a degree necessary to meet all the requirements of the human cornea.

The invention is illustrated by the Examples which follow. All parts and percents referred to herein are on a weight basis and all viscosities measured at 25°C. unless otherwise specified.

EXAMPLE 1

557 g of 1,3 - bis(4 - hydroxybutyl) tetramethyl disiloxane, 634 g of dry pyridine and 2 liters of hexane are charged to a 5 liter reaction flask equipped with a mechanical stirrer and drying tube. The mixture is chilled to 0°C and then 836 g of methacryloyl chloride is added drop wise. The mixture is agitated continuously overnight. The reaction solution is extracted consecutively with 10% water solutions of HCl and NH₃ in order to remove excess reagents and pyridine hydrochloride. The resulting solution of the product in hexane is dried with anhydrous MgSO₄, filtered, and solvent removed at reduced pressure. About 459 g (55% yield) of 1,3 - bis(4 - methacryloxy butyl) tetramethyl disiloxane is collected. The structure is confirmed by infrared spectra, proton magnetic resonance spectra and elemental analysis. IR spectra shows no intense hydroxyl band between 3100 and 3600 cm⁻¹ but does show strong methacrylate absorptions at 1640 and 1720 cm⁻¹. PMR spectra agreed with the proposed structure:



1,3 - bis(4 - methacryloxy butyl) tetramethyl disiloxane.

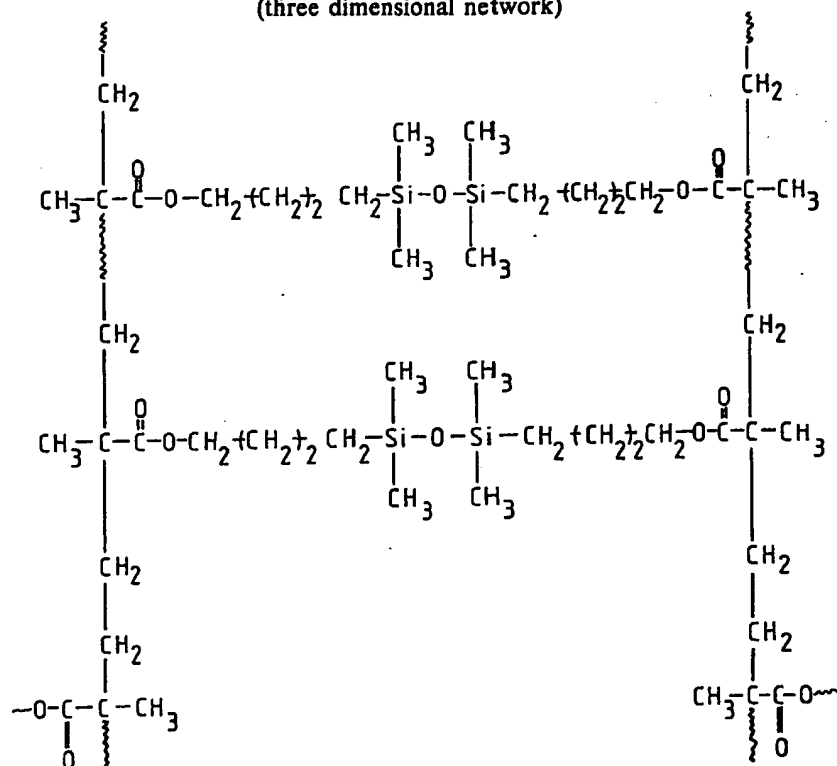
| | Proton | ppm | Integrated Area | Multiplicity | |
|----|----------------|------------------|-----------------|--------------|----|
| 5 | H ¹ | 7.0 _s | 1 | singlet | 5 |
| | H ² | 6.5 _s | 1 | singlet | |
| | H ³ | 3.0 _s | 3 | singlet | |
| | H ⁴ | 5.1 _s | 2 | triplet | |
| | H ⁵ | 2.7 | 4 | multiplet | |
| 10 | H ⁶ | 1.6 _s | 2 | triplet | 10 |
| | H ⁷ | 1.2 _s | 6 | singlet | |

Elemental analysis gave 13.6% Si (calc. 13.5%), 58.1% C (calc. 57.9%), and 9.4% H (calc. 9.2%). The product was a clear, colorless, fragrant fluid.

EXAMPLE 2

The fluid product of Example 1 is placed between glass plates with 0.2% benzoin methyl ether and irradiated with UV light at room temperature. A colorless, optically clear, hard, highly crosslinked film is obtained. The following is a representation of the cross-linked polymer.

(three dimensional network)



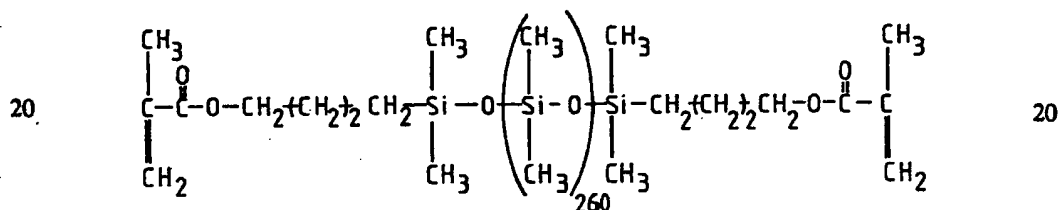
EXAMPLE 3

489.75 g of octamethylcyclotetrasiloxane and 10.25 g of 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane are charged into a reaction vessel equipped with a mechanical stirrer. About 25 g of Fuller's Earth and 1.35 ml of conc. H_2SO_4 are mixed and added to the vessel with continuous stirring while bubbling dry N_2 through the reaction mixture. The charge is warmed to $60^\circ C$ and stirred for two days, at which time the viscous fluid is neutralized with Na_2CO_3 , diluted with hexanes, and filtered. The hexanes/monomer solution is washed with water, dried with $MgSO_4$ (anhydrous) and solvent removed at reduced pressure. Low molecular weight unreacted cyclic siloxanes are removed by heating the monomer to $110^\circ C$ at 0.2 mm Hg in a rotary evaporator. The product obtained is an odorless, colorless, clear fluid of 8.5 stokes viscosity measured in Gardner Viscosity tubes. The monomer comprised about 260 repeating



units. Fluid collected during the devolatilizing of the product shows no methacrylate absorptions in IR spectra and could not be cured.

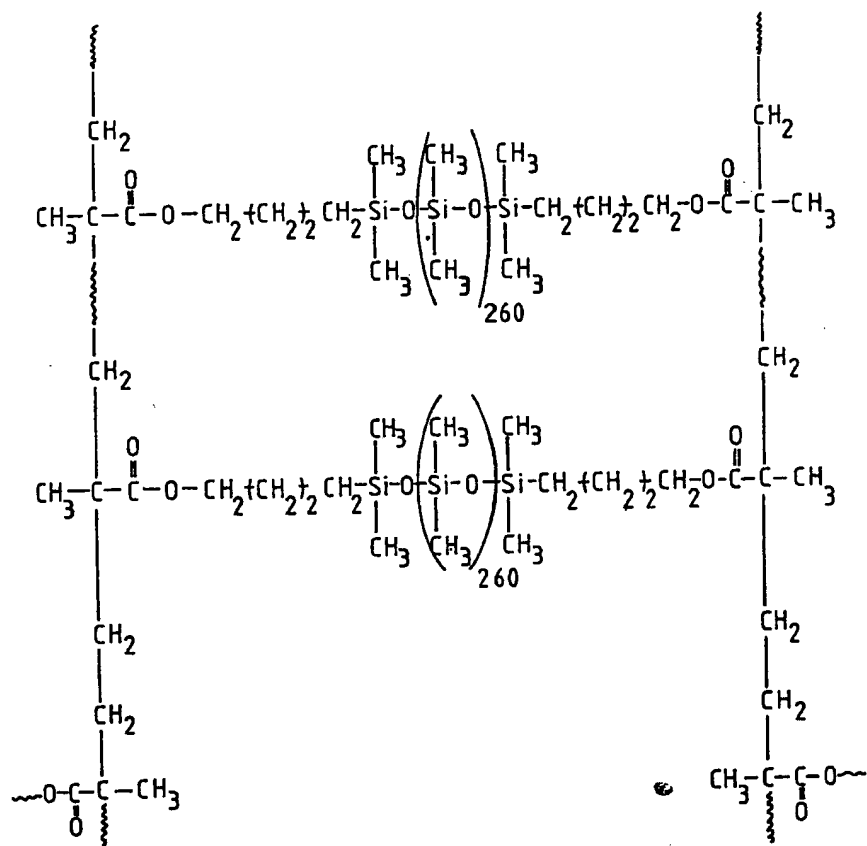
IR spectra of the monomer shows a slight methacrylate absorption and broad siloxane absorptions between 1000 and 1100 cm^{-1} , indicative of linear poly(dimethyl siloxanes) with the following formula:



EXAMPLE 4

Films of the fluid product of Example 3 are cast between glass plates by adding 0.2% bis(isobutyl) peroxy dicarbonate to the monomer and heating for 1/2 hour at $40^\circ C$, 1/2 and $60^\circ C$ and 1/4 hr. at $80^\circ C$. The glass plates are separated. The films are then kept at $80^\circ C$ for 15 minutes. Colorless optically clear, odorless, elastic and strong films are obtained such as represented by the three dimensional network polymer below. The following physical properties are measured on an Instron tester ASTM D1708, no conditioning, using standard "dog bone" samples cut from 0.2 mm thick films. The speed is 0.25 inches per minute. This test is used on all the Examples where tensile strength, modulus and elongation are measured.

(three dimensional network)



Tensile strength
Tensile modulus
Elongation

150 g/mm²
72 g/mm²
177%

5

5

EXAMPLE 5

The fluid product of Example 3 together with 0.2% di(sec - butyl) - peroxydicarbonate is placed in a suitable contact lens spin casting mold and spin cast under polymerizing conditions to a contact lens such as taught in U.S. patent 3,408,429. The lens is optically clear, elastic and strong.

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EXAMPLE 6

About 97.3 g of octamethyl cyclotetrasiloxane, 2.7 g of 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane and 0.6 ml of trifluoromethyl sulfonic acid are charged to a pressure bottle, sealed and shaken for 24 hours. The viscous monomer fluid obtained is neutralized with sodium carbonate and diluted with hexanes. The monomer/hexanes solution is washed with water, dried with anhydrous MgSO₄ and the solvent removed at reduced pressure. Volatiles are removed from the monomer at 0.2 mm Hg and 110°C using a wiped film still. High pressure gel permeation chromatography of the product shows essentially total removal of low molecular weight volatile material. The product is a colorless, clear, odorless fluid of 4.4 stokes viscosity measuring in Gardner viscosity tubes.

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EXAMPLE 7

Films are made from the viscous fluid product of Example 6 using procedures similar to Example 4. The films obtained comprise about 200 repeating

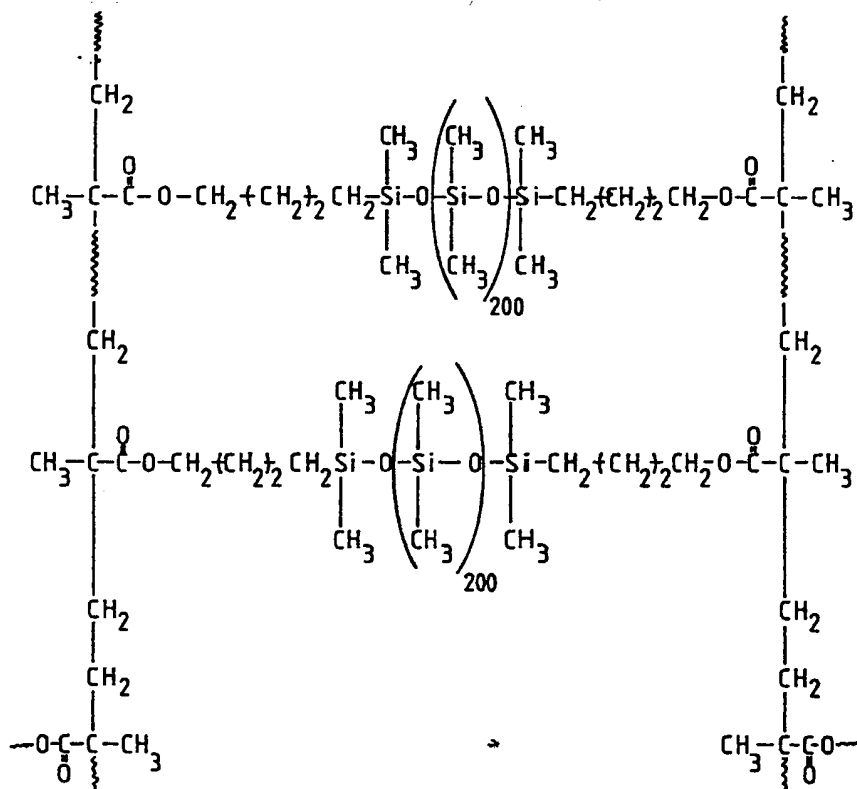
25



25

units, and are represented by the three dimensional network polymer below:

(three dimensional network)



IR spectra are similar to those taken in Example 3.

The films are tested, ASTM D1708, giving the following results:

| | |
|------------------|-----------------------|
| Tensile strength | 159 g/mm ² |
| Tensile modulus | 104 g/mm ² |
| Elongation | 151% |

EXAMPLE 8

The viscous fluid product produced in Example 6 is mixed with 2.0% benzoin butyl ether. About 30 μ l of the mixture is placed in a spinning contact lens mold under N₂ atmosphere. After 20 minutes irradiation with UV light, a cured contact lens is obtained. The lens formed is optically clear, elastic and strong.

EXAMPLE 9

Ten (10) parts of allylmethacrylate monomer and four tenths (0.4) of a part of t-butyl peroctoate are added to ninety (90) parts of the fluid product obtained in Example 3. The reaction mixture is placed into a casting cell which is then placed into an 80°C oven for half an hour. The temperature is thereafter raised to 100°C and maintained at 100°C for one hour. An optically clear film is removed from the cell and kept at 80°C for 15 minutes.

The above is repeated by reacting the product of Example 3 with several other monomers as shown in Table I. The percent shown in Table I is the percent of comonomer used. The properties of the copolymers are outlined in Table I.

As illustrated in Table I, it is one advantage of the instant invention to be able to increase the tensile strength and elongation while retaining sufficient oxygen transportability. One problem with the prior art silicone polymers is that these polymers are not very strong and have poor tear strength and poor tensile strength. One of the problems with the PHEMA (control) is that contact lenses made from

this material do not have the necessary oxygen transporting properties to meet all the requirements of the human cornea. As mentioned, the oxygen requirement of the human cornea is about 2×10^{-6} cm³/(sec. cm² atm). Table I illustrates the effect the instant co-monomers have on the strength of the polymers of the instant invention. There is an improvement in tensile strength with the use of the instant monomers.

In the case of modulus, it would be most preferred if the modulus is below 300 in order to obtain a soft contact lens; generally the lower the modulus the softer the contact lens.

As to elongation, it is generally preferred that elongation be as high as possible.

As to oxygen transport, it is desirable that this rate be maximized. This rate should be greater than the rate of oxygen required by the human cornea.

The tensile strength test, modulus test and elongation test are measured, as mentioned, on an Instron Tester ASTM D 1708 using standard "dog bone" samples cut from 0.2 mm thick films. There is no conditioning and the speed is 0.25 inches per minute.

The Oxygen Transport Rate was determined by the following technique. This test is measuring the oxygen permeability of a material while it is wet with water. This is an attempt to closely reproduce the same conditions which exist in the human eye when fitted with a contact lens. Two chambers filled with water at 32°C are connected together by a common passageway over which is placed the material to be tested. Nitrogen-purged water is pumped into both chambers until the oxygen concentration is very low (~0.04 ppm). Then air water (oxygen concentration ~8 ppm) is introduced into the lower chamber. There is located in the upper chamber an oxygen sensing electrode which measures the diffusion of oxygen from the lower chamber through the membrane being tested and into the upper chamber. This measures apparent oxygen transport rate of the material covering the passageway between the two chambers.

TABLE I

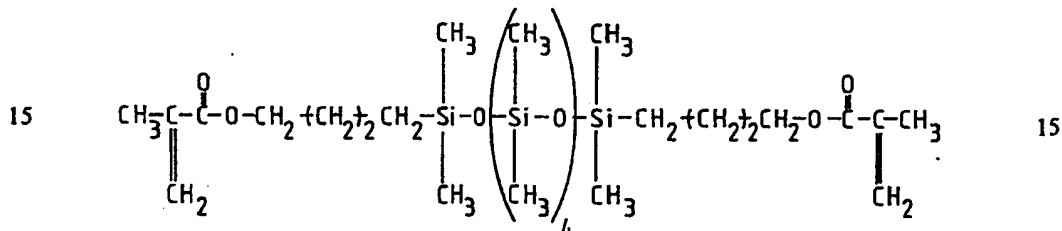
| | | Tensile Strength (g/mm ²) | Modulus (g/mm ²) | Elongation (Percentage) | Approximate *Apparent O ₂ Transport Rate |
|--------------------------|-----|---|---------------------------------|----------------------------|--|
| PHEMA | | 40 | 40 | 150 | 4×10^{-7} |
| Allyl methacrylate | 10% | 71 | 143 | 65 | 62×10^{-7} |
| Butoxyethyl methacrylate | 10% | 26 | 42 | 100 | 50×10^{-7} |
| Butoxyethyl methacrylate | 30% | 31 | 38 | 136 | |
| Cyclohexyl methacrylate | 10% | 70 | 75 | 131 | 56×10^{-7} |
| Ethyl methacrylate | 10% | 67 | 80 | 136 | 54×10^{-7} |
| Methyl methacrylate | 10% | 100 | 90 | 145 | |
| Ethyl hexyl acrylate | 10% | 50 | 73 | 110 | 54×10^{-7} |
| Ethyl hexyl acrylate | 30% | 41 | 69 | 105 | |
| n bu acrylate | 10% | 49 | 79 | 110 | |
| n bu acrylate | 30% | 30 | 79 | 58 | 50×10^{-7} |
| bu acrylate | 10% | 51 | 78 | 116 | 58×10^{-7} |
| bu acrylate | 30% | 37 | 80 | 82 | |

$$\text{*Apparent Oxygen Transport Rate} = \frac{\text{cm}^3(\text{O}_2)}{\text{sec-cm}^2\text{-atm}}$$

EXAMPLE 10

58.3 g of 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane, 41.7 g of octamethyl cyclotetrasiloxane, 1 ml concentrated H_2SO_4 and 2 gm of Fuller's earth are charged into a pressure flask. After two days equilibration the mixture is neutralized with Na_2CO_3 , filtered, diluted with hexanes, washed with water, dried, and the solvent removed at reduced pressure. The monomer product as illustrated below was a colorless, odorless fluid with low viscosity as measured in Gardner Viscosity tubes.

10 g of monomer product is mixed with 0.1 wt. % benzoin methyl ether and 0.1 wt % azobis(isobutyronitrile). The initiator-monomer solution is poured into button molds and cured for 20 minutes under UV light in a nitrogen atmosphere and thereafter followed by 30 minutes at $80^\circ C$ in air. The buttons are optically clear, colorless, hard and tough. Contact lenses are lathed from these buttons. The following is the formula for the above monomer:



EXAMPLE 11

7 g of the monomer product produced in Example 10 and 3 g of N-vinylpyrrolidone are mixed with 0.1 wt. % benzoin methyl ether and 0.1 wt. % azobis(isobutyronitrile). The initiator-monomer-comonomer solution is cured as described in Example 10.

The copolymer buttons obtained are optically clear, colorless, hard and tough. The lathing of the buttons to contact lenses is substantially easier than the lathing of Example 10 buttons.

EXAMPLE 12

30% tetrahydrofurfuryl methacrylate (TFM) is copolymerized with 70% monomer of Example 10 in suitable molds. The buttons obtained are optically clear, colorless, hard and tough. The TFM copolymer buttons are lathe cut into contact lenses.

EXAMPLE 13

99.3 g of octamethyl cyclotetrasiloxane, 0.7 g of 1,3 - bis(4 - methacryloxybutyl) tetramethyl disiloxane, and 0.3 ml of trifluoromethyl sulphonic acid are charged to a pressure bottle. The bottle is sealed and shaken for five days. The monomer fluid obtained is neutralized with sodium carbonate and diluted with hexanes and filtered. The monomer/hexanes solution is washed with water, dried over $MgSO_4$, and the solvent removed at reduced pressure. Volatiles are removed from the prepolymer at 0.2 mm Hg pressure and $110^\circ C$. High pressure gel permeation chromatography of the product shows all low molecular weight volatile material is removed. The product is a colorless, clear, odorless fluid of very high viscosity with about 800 repeating



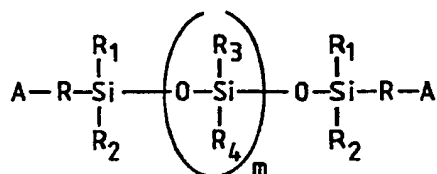
units. The following is a formula for the above monomer.

removed at reduced pressure. The product is siloxane monomer consisting of 5 mole % phenyl substituted siloxane units and 95 mole % methyl substituted siloxane units. An infrared spectrum of the monomer product shows sharp weak absorptions at 700, 1430, 1590 and 3050 cm^{-1} and a shoulder on the broad Si-O-Si absorption at 1125 cm^{-1} . These are characteristic of phenyl and silicone phenyl groups. The product is colorless, transparent, odorless, and viscous. The viscosity is 17 stokes as measured in the Gardner Viscosity tubes. It is cast into elastic, transparent films using procedures similar to Example 4.

WHAT WE CLAIM IS:—

1. A polysiloxane polymer formed by polymerizing one or more poly(diorganosiloxane) or linear poly(organosiloxane) monomers α,ω -terminally bonded through divalent hydrocarbon groups of at least three carbon atoms to activated unsaturated groups (as herein defined), optionally with one or more free-radical polymerizable co-monomers, to form a cross-linked three-dimensional polymeric network.

2. A polysiloxane polymer according to Claim 1, wherein said poly(diorganosiloxane) or linear poly(organosiloxane) has the formula



wherein A is an activated unsaturated group (as herein defined), R is a divalent hydrocarbon radical having from 3 to 22 carbon atoms, R_1 , R_2 , R_3 and R_4 can be the same or different and are monovalent hydrocarbon radicals or halogen substituted monovalent hydrocarbon radicals, each having from 1 to 12 carbon atoms and m is 0 or greater.

3. A polysiloxane polymer according to Claim 2, wherein A is 2-cyanoacryloxy, acrylonitril, acrylamido, acryloxy, methacryloxy, styryl, N-vinyl - 2 - pyrrolidinone - 3 - yl, N - vinyl - 2 - pyrrolidinone - 4 - yl or N - vinyl - 2 - pyrrolidinone - 5 - yl and R is an alkylene radical and R_1 , R_2 , R_3 and R_4 are alkyl radicals, having from 1 to 10 carbon atoms each.

4. A polysiloxane polymer according to Claim 2, or Claim 3 wherein m is a number from 0 to 800.

5. A polysiloxane polymer according to Claim 4, wherein m is from 0 to 200.

6. A polysiloxane polymer according to Claim 5, wherein m is a number from 0 to 50.

7. A polysiloxane polymer according to Claim 6, wherein m is a number from 0 to 25.

8. A polysiloxane polymer according to Claim 4, wherein m is 50 or greater.

9. A polysiloxane polymer according to Claim 8, wherein m is from 50 to 800.

10. A polysiloxane polymer according to any one of Claims 3—9, wherein said alkylene radical has 3 or 4 carbon atoms.

11. A polysiloxane polymer according to any one of Claims 3—10, wherein R_1 — R_4 are selected from methyl and phenyl radicals.

12. A polysiloxane polymer according to Claim 11, wherein R_1 — R_4 are all methyl radicals.

13. A polysiloxane polymer according to any preceding claim, wherein said poly(diorganosiloxane) or linear poly(organosiloxane) is copolymerized with one or more monomers selected from lower esters of acrylic or methacrylic acid, a styryl, and N-vinyl pyrrolidinone.

14. A polysiloxane polymer according to Claim 13, wherein the co-monomers are selected from styrene and N-vinyl pyrrolidinone.

15. A polysiloxane polymer according to Claim 13, wherein the co-monomer is selected from allyl methacrylate, butoxyethyl methacrylate, cyclohexyl methacrylate, ethyl methacrylate, methyl methacrylate, ethylhexyl acrylate, *n*-butyl acrylate, and *n*-butyl methacrylate.

16. A shaped article suitable for use in biomedical applications and being formed from a polysiloxane polymer according to any preceding claim.

17. A hydrolytically stable, biologically inert, transparent contact lens or

contact lens blank having sufficient oxygen transportability to meet the requirements of the human cornea, the lens or lens blank being formed from a polysiloxane polymer according to any one of Claims 1—15.

5 18. A contact lens or lens blank according to Claim 17 which has a Shore hardness of above 60 on the Shore hardness scale A. 5

19. A contact lens or lens blank according to Claim 17 which has a Shore hardness of 60 or below on the Shore hardness scale A.

20. A contact lens or lens blank according to Claim 19, which has a Shore hardness of 25 to 35 on the Shore hardness scale A.

10 21. A contact lens or lens blank according to any one of Claims 17—20 which has an oxygen transportability of at least 2×10^{-8} cm³/(sec.cm²atm). 10

22. A contact lens or lens blank according to any one of Claims 17—21 which has a tensile modulus of elasticity of 400 g/min² or less.

15 23. A contact lens or lens blank according to any one of Claims 17—22, wherein the lens is made by spin casting. 15

24. A method of making a contact lens or lens blank according to Claim 23, which comprises placing the polymerizable monomer or monomers and an initiator selected from free radical initiators and U.V. initiators in a spin casting contact lens mold, and subjecting the reaction mixture to polymerization while spin casting to thereby form the contact lens or lens blank. 20

25. A polysiloxane polymer according to Claim 1 and substantially as described in any one of Examples 2, 4, 5, 7—12, 14 and 15 herein.

26. A shaped article suitable for use in biomedical applications, according to Claim 16 and substantially as described in any one of Examples 2, 4, 5, 7—12, 14 and 15 herein. 25

27. A contact lens or lens blank according to Claim 17 and substantially as described in any one of Examples 5, 8 or 10—12.

28. A method of making a contact lens or lens blank according to Claim 24 and substantially as described in either one of Examples 5 and 8 herein.

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